BEHAVIOR OF METHYLOLMELAMINE-TREATED COTTON UNDER ENVIRONMENTAL STRESS

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The rot resistance and weather resistance of cotton treated with 12% methylolmelamine by the formic acid-colloid process was extensively evaluated in soil burial, outdoor exposure and Weather-Ometer studies.

More than a year of outdoor weathering was required before a significant loss of breaking strength could be observed. Other characteristics change more quickly, however, and provide a more sensitive index of actinic degradation. Significant changes in the load-elongation curves of fabric strips were observed after two months' exposure. Nitrogen determinations indicated that most of the resin had disappeared prior to any strength loss. The most sensitive measurement of actinic effects was the conversion of the treated fabric from a cuprammonium-insoluble material to a cuprammonium-soluble product. This reaction was 50% complete in only five months.

These reactions differentiate between actinic damage and microbiological attack, since deterioration in soil burial occurred before much of the resin was lost and before more than 10% of the material was converted to a cuprammonium-soluble product. The rot resistance of this fabric is, however, much greater than can be obtained with conventional fungicides. In soil burial, no loss of breaking strength occurred for 64 weeks. In fact, the original loss in strength caused by the resin treatment was totally regained during this interval.

Basic differences between outdoor weathering and exposure in a Weather-Ometer were also found. As opposed to outdoor weathering, a loss of breaking strength in the Weather-Ometer preceded any change in the load-elongation curve.

Microscopical studies indicated that the removal of resin in both soil burial and weathering began at the periphery of the fibers. The peripheries of many fibers were exposed without imparing microbiological resistance; hence, resistance cannot be due to a mechanical barrier.

INTRODUCTION

THE use of a formic acid colloid of methylolmelamine as a weather- and rot-resistant finish for cotton was introduced by Berard *et al* in 1959 (*1*) and discussed in further detail in 1961 (*2*). In a study of application techniques, they established that the degree of rot resistance depended on the age of the acid-colloid solution and upon the amount of resin in the fabric. Colloidal solutions of trimethylolmelamine containing 20% formic acid were stable for about eight hours. However, the degree of rot resistance was sharply reduced if the colloid was allowed to age longer than two hours before being used, or if less than 10% resin solids were deposited in the fabric. Cotton print cloth finished with 12% of freshly prepared resin lost considerable strength due to the treatment; but no further loss of tensile strength occurred during the entire 21-week duration of their soil-burial experiment.

The selection of formic acid by Berard was made only after extensive studies of a number of acid-colloid systems. Cotton fabric was rot resistant when treated with an aqueous solution of trimethylolmelamine which had been acidified immediately before use with acetic acid and a metal salt. This solution, however, is very unstable and insoluble polymer begins to precipitate within 30 minutes after addition of the acid. Glycolic acid solutions of trimethylolmelamine are also unstable. Lactic acid forms a stable colloid, but imparts much less rot resistance to cotton fabric.

Berard's application studies can be summarized by stating that the best rot resistance is obtained when fabrics are treated with a freshly prepared colloidal solution containing enough trimethylolmelamine and formic acid (in a molar ratio of about 1:5), to provide at least 12% add-on of resin. The treatment of the fabric involves a simple pad, dry and cure operation as normally required for resin applications. The soil-burial experiments carried out by Berard are proof that the degree of rot resistance obtained by this treatment is comparable to the rot resistance of cotton which has been chemically modified by acetylation and cyanoethylation, and superior to that obtained by any of the commonly used textile fungicides. The 21-week burial period, however, is insufficient to determine the ultimate rot resistance of the methylolmelamine-treated fabric or to judge between any of the chemically modified cottons.

Berard also found that the resistance to outdoor weathering is improved by the acid-colloid finish (*2*). After 12 months' exposure at New Orleans, La, treated fabrics

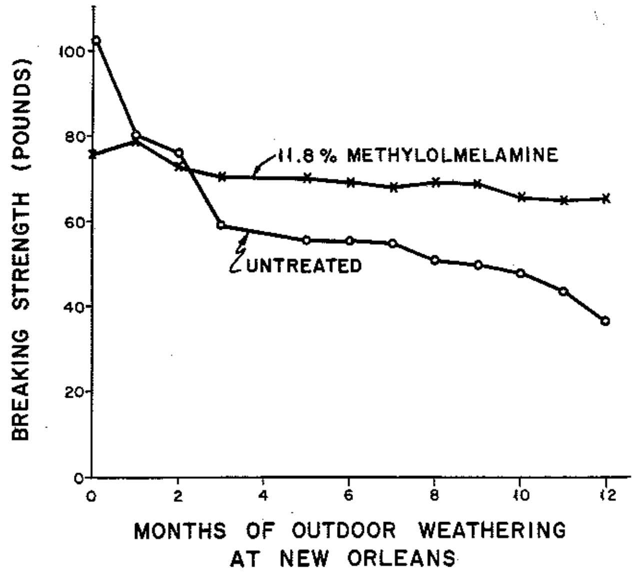

Figure 1
Effect of outdoor weathering at New Orleans on tensile strength of cotton duck treated with 12% formic acid colloid of methylolmelamine, and untreated fabric.

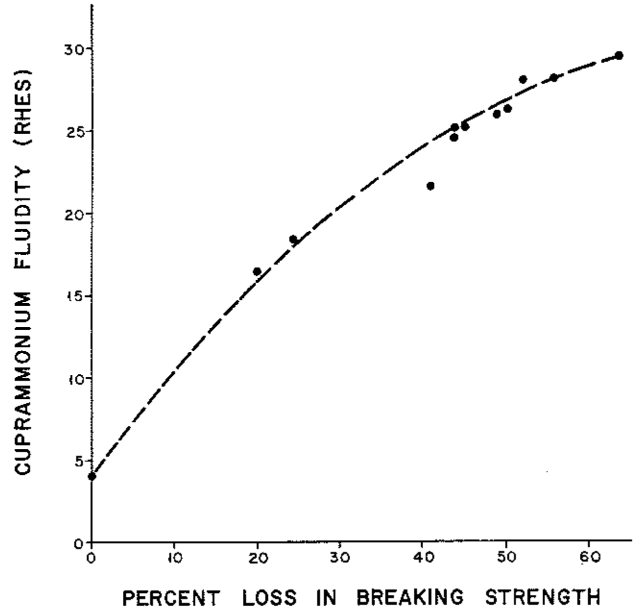

Figure 2
Relationship between cuprammonium fluidity and breaking strength of untreated cotton duck after outdoor weathering at New Orleans.

containing as little as 6% resin had retained all of their original tensile strength. Untreated fabric lost about half of its original tensile strength in the same period. The use of aminoplast resins as weather-protective finishes has been reported by several investigators (5); and Berard was not able to claim any advantage in weather resistance for his formic acid-colloid process over trimethylolmelamine applied by the conventional technique because the treated fabrics had not been exposed outdoors long enough to fully assess their maximum durability to weather. Furthermore, it was not determined whether the treatment offered protection from actinic effects or whether the observed resistance to weathering was merely another manifestation of rot resistance.

A study of the changes in fungus-proofed textiles during exposure to microbiological attack is the subject of a previous report from this laboratory (7). It was found that the deterioration of treated fabric in soil burial is a two-phase process. In the first phase, there is no loss of tensile strength by the fabric. The duration of this phase depends on the initial concentration of fungicide and its rate of loss from the fabric. The second stage is marked by the rapid deterioration of the fabric; but this begins only after the fungicide content has been reduced to a level at which the material is no longer protected. It was therefore advocated that more attention be given to the durability of the treatment on the fabric, and less to the rate of tensile strength loss which occurs only when the treatment is no longer effective.

This paper contains extended soil-burial and weathering data of a cotton fabric treated under Berard's optimum conditions. Proof of the resistance of this fabric to actinic damage is included. In conformance with our position, as previously advocated (7), the main body of this report is a study of some of the changes in the treatment and the treatment-substrate complex which were observed before any loss of tensile strength could be detected.

MATERIALS AND METHODS

FABRIC DESCRIPTION——The fabric used in these experiments was the "standard" blue-line eight-ounce cotton duck described by Shapiro (*12*). Fifty yards of this fabric were treated with the formic acid colloid of methylolmelamine at the Southern Regional Research Laboratory of the U S Department of Agriculture, New Orleans, La. It was reported to contain 11.8% resin on the basis of a nitrogen determination.

EXPOSURE TESTS——Some of the treated material was cut into 1¼-inch strips, ravelled to 55 threads and buried in soil in accordance with method 5762 or Federal Specification CCC-T-191b (*14*). Since the durability of the material was unknown, the exposure periods were varied in order to obtain the most data from the available fabric. Consequently, 10 strips were withdrawn at irregular intervals depending on the rate of change in the properties of the material.

Outdoor exposure tests were conducted at New Orleans, and at Maynard, Mass. Both locations are unshaded, and the samples were tacked on open-backed wooden racks facing south at an angle of 45° from the vertical and at a minimum distance of 30 inches above the ground. Weathered samples were removed every four weeks and ravelled into standard 1x6-inch strips.

Other 1x6-inch strips were exposed in a Weather-Ometer according to method 5804 of Specification CCC-T-191b, for periods of 100, 200 and 500 hours. This test was run without the water-spray cycle, to separate actinic effects from leaching. Because of space limitations, there were only three strips for each exposure period.

Untreated samples of blue-line fabric were included in all exposure tests.

TEST METHODS——All fabrics were conditioned for 24 hours at 70 ± 2°F and 65 ± 2% RH before testing. The results of chemical analyses therefore contain a small but constant error due to moisture content. Breaking strengths of all 1x6-inch ravelled warp specimens were determined with an Instron tensile tester, Model TT-C1, as described in method 5104.1 of Federal Specification CCC-T-191b. The complete load elongation curves were also recorded from the Instron charts. The specified gage length of three inches and pulling speed of 12 inches per minute results in a rate of elonga-

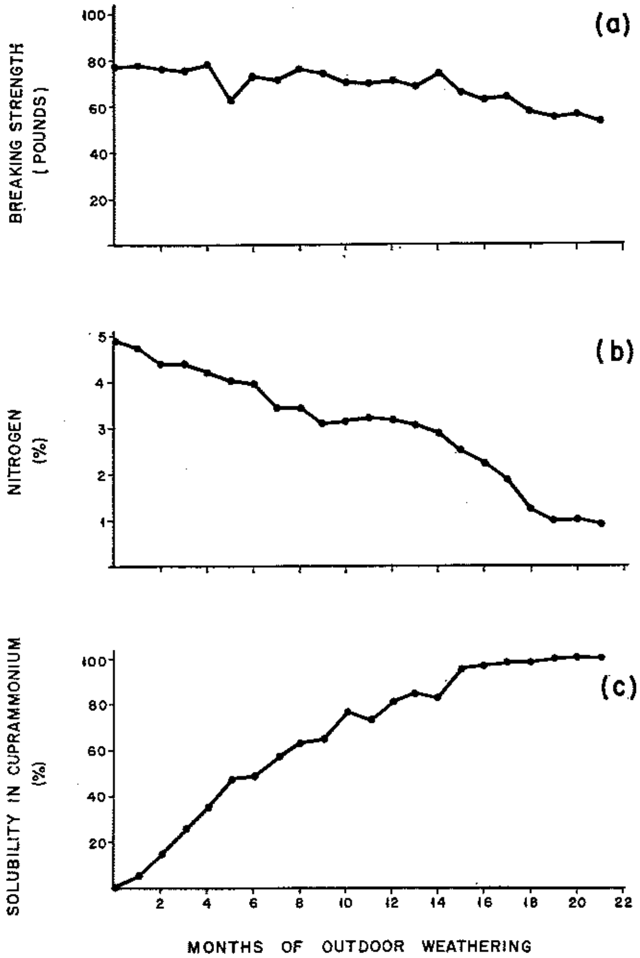

Figure 3
Effect of outdoor weathering at Maynard, Mass, on: a) breaking strength; b) nitrogen content; and c) cuprammonium solubility of methylolmelamine-treated cotton duck.

tion of 400%. Each load elongation curve in this report represents the one strip closest to the mean value for the 10 strips in its group. Details of this procedure and definitions of terms can be found in Susich and Backer's basic reference (*13*).

Nitrogen content was usually determined colorimetrically by the Kjeldahl-Nessler procedure of Miller and Miller (*10*). For the Weather-Ometer experiment, nitrogen was determined titrimetrically after distillation in a Thomas-ASTM micro Kjedahl apparatus. To determine extractable nitrogen, approximately 0.5 gm of material was cut into ⅛-inch squares, added to 10 ml of water and the water brought to boil. The material was extracted with three 10-ml aliquots of boiling water before determining residual nitrogen. Where applicable, the viscosity in cuprammonium hydroxide was determined with Shirley X-type viscometers and the method currently used by the British Cotton Industry Research Association (*3*). The cuprammonium reagent contained 15.0 ± 0.1 grams per liter copper and 200 ± 10 grams per liter ammonia (NH_3). Cotton treated with the formic acid colloid of methylolmelamine is insoluble in cuprammonium. Changes in the percent solubility in this reagent, however, were determined by the method of Mehta and Mehta (*8*). This method proved to be relatively precise. Replicate determinations seldom varied by more than 1%.

Microscopic studies were also carried out by G Susich of this Division. Samples of fabric before and after exposure were dyed in a bath containing 2% Direct Brilliant Sky Blue 6B (CI Direct Blue 1), 2% Kiton Yellow T (CI Acid Yellow 23), 25% Glauber salt (on weight of fabric) and 10% acetic acid (on weight of fabric). The fabric was boiled for 30 minutes in a liquor/cloth ratio of 50:1. This test permits differentiation between untreated cellulose which dyes blue, and resin-treated cellulose which dyes yellow.

RESULTS AND DISCUSSION

OUTDOOR EXPOSURE AT NEW ORLEANS, LA ——The breaking-strength data for the New Orleans exposure test are presented in Figure 1. Within two months, the initial loss of tensile strength caused by the resin treatment was more than offset by the rapid decrease in tensile strength of the untreated material. After 12 months, the tensile strength of the treated material was relatively unchanged; but the untreated material had lost over 60% of its strength. These results are similar to Berard's (*2*) and serve to corroborate his claim that the methylolmelamine finish is resistant to outdoor exposure. These data alone, however, are not proof that the treated fabric was protected from actinic degradation, since the untreated material may have been degraded primarily by microorganisms.

Consequently, the viscosity in cuprammonium hydroxide was used to establish the mode of breakdown in the untreated fabric. According to Howard and McCord (*6*), when actinic effects are predominant, the cuprammonium fluidity of untreated cotton should increase to almost 30 rhes by the time the tensile strength has decreased by 50%. Untreated cotton exposed in a location where microbial attack is predominant should show no increase in fluidity, within experimental limits, even after 80% of the tensile strength has been lost.

The viscosity vs tensile strength curve (Figure 2) is comparable to Howard and McCord's curve for untreated material degraded by sunlight. It is therefore concluded that the degradation of the untreated material in Figure 1 is accomplished primarily by sunlight and not by microorganisms. Since the treated material is not similarly degraded, it must be resistant to actinic damage. A similar argument has been employed by Dean et al (*5*) to prove that urea-formaldehyde-treated fabric is resistant to sunlight. This proof should accompany every claim of resistance to actinic effects, where there is any possibility of microbial degradation.

The need for studies of early changes in the treatment or the treatment-fabric complex is evident from Figure 1. If weather-resistant treatments of this type are to be evaluated solely on the basis of tensile loss in the base fabric, exposure periods of more than one year are required. Therefore, an attempt was made to find a more sensitive test for actinic effects. This study was performed on fabrics weathered at Maynard, Mass, where an exposure test of almost two years was conducted.

OUTDOOR EXPOSURE AT MAYNARD, MASS—— The original tensile loss caused by the resin treatment was once again offset in less than two months outdoor exposure by the rapid deterioration of the untreated material. The tensile strength of the untreated material had dropped to 68 pounds in two months; hence the exposure of untreated samples was terminated. During the two-year period, the treated material lost about 30% of its tensile strength, but the rate of loss was barely perceptible from month to month, as shown in Figure 3a.

The slow change in the strength of the base fabric gave no indication of the significant changes which were occurring in the treatment and the treatment-fabric complex. The loss of resin was almost complete in 21 months as measured by nitrogen content (Figure 3b);

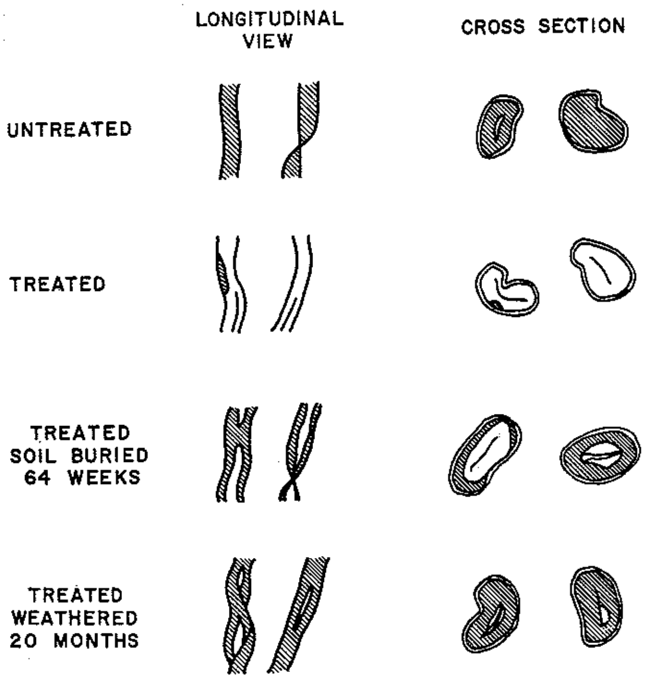

Figure 4
Schematic diagrams of cotton fibers (of approximately 25μ diameter) showing deposition of methylolmelamine in the formic-acid-colloid process; and mode of resin removal during outdoor weathering and soil burial.

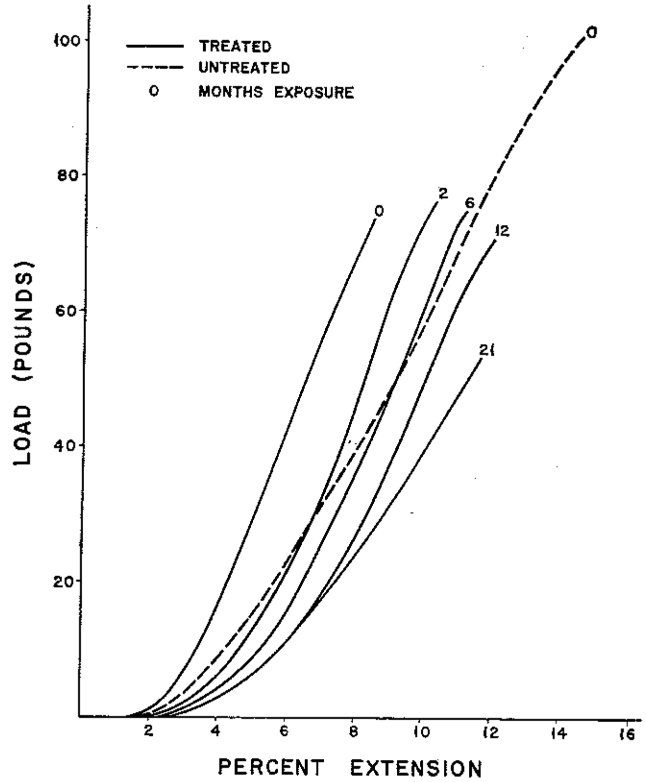

Figure 5
Changes in the load-elongation curve of methylolmelamine-treated cotton duck during outdoor weathering at Maynard, Mass.

or as observed microscopically (Figure 4). The results obtained by dye studies were radically different from Berard's (*2*) results based on solubility in cupriethylenediamine hydroxide. Berard concluded that fibers treated with the fresh acid colloid of methylolmelamine had the resin deposited primarily in the outer portion of the cell wall. The innermost sections of the fiber responded to cupriethylenediamine hydroxide by nonhomogeneous solution in a manner similar to that observed for cotton having small amounts of bound formaldehyde. In our dye test, untreated cotton is dyed blue, while heat-cured resin-treated cotton is dyed yellow. Except for a few small blue points, fibers removed from formic-acid-colloid-treated fabric were dyed uniformly yellow when examined either longitudinally or in cross section. This would indicate that the resin was uniformly dispersed throughout the fibers. These differences may be reconciled if it is assumed that the resin which penetrates to the innermost part of the fiber is either the monomeric form or a decomposition product such as formaldehyde, which is capable of prohibiting the reaction between the blue dye and cellulose, but does not affect the solubility in cupriethylenediamine.

After 20 months' outdoor exposure, most of the yellow-dyed resin had disappeared. Many fibers were stained completely blue. Evidently the resin is progressively removed from the periphery of the fibers, because the resin which remains is primarily in the innermost parts of the fiber, as shown in Figure 4.

If the microbiological resistance of resin-treated fabrics is due solely to the physical presence of the resin, the rate of loss of nitrogen can provide an estimate of the durability of the treatment. There is general agreement, however, that protection from microbiological deterioration involves more than the amount of resin and includes the reactivity of cellulose toward microbial enzymes. There is some dispute over whether the change in the reactivity of the cellulose is brought about by chemical reaction or whether the resin acts simply as a physical barrier. The fact that resin-treated cotton is insoluble in cuprammonium was originally believed to be related to crosslinking, since simple substitution of cellulose hydroxyl groups by monofunctional agents (ie, those which react with only one hydroxyl group with no possibility of crosslinking) did not result in loss of solubility (*11*). Mehta and Mehta (*9*) subsequently found that cellulose became insoluble when treated with certain monofunctional agents, such as the H-type Procion fiber-reactive dyes. Hence, solubility in cuprammonium hydroxide is currently believed to be a function of the molecular configuration of the substituent group. During weathering, the fabric treated with the formic acid colloid of methylolmelamine becomes completely soluble in cuprammonium after 19 months' exposure (Figure 3c). This change in solubility is a direct indication of an alteration in the resin-fabric bond, and a measure of the increase in reactivity of the cellulose. It is anticipated that changes of this type will eventually prove to be more indicative of the durability of the rot-resistant finish than nitrogen content.

Recording the load-elongation curves provides additional information when an Instron is used to determine breaking strength. According to Cooke, et al (*4*), stress-strain measurements can be made either on the fabric or the yarn. Typical load-elongation curves of 1x6-inch strips of fabric exposed to weathering are presented in Figure 5. Comparison of the unexposed samples shows that the formic-acid-colloid finish causes a marked decrease in elongation in addition to the decrease in ultimate breaking strength. This was observed by Cooke (*4*) and was thought by him to be the result of crosslinking. Even though the breaking strength of the treated samples did not change appreciably during weathering, the elongation at loads less than breaking strength progressively increased, and eventually became greater than the elongation of untreated, unexposed fabric.

The increase in elongation during the weathering of untreated fabrics probably indicates that crosslinks are being broken, but a complete interpretation of these changes requires a separate study. In particular, the loss of elasticity, as defined by Cooke (4), is undoubtedly more important than the simple loss of elongation. Preliminary studies indicate that the elongation of untreated fabric also increases during weathering. A more detailed study of stress-strain curves will not be undertaken until the broader applicability of this approach to other resin-fabric systems is ascertained.

The rot resistance decreases steadily during weathering; hence the simple practice of carrying out soil-burial studies on weathered fabric provides a more sensitive indicator of actinic damage than prolonged weathering alone. A significant change in rot resistance may be detected after only 10 months' weathering followed by 12 weeks of soil burial, as shown in Table I.

TABLE I
Rot resistance of methylolmelamine-treated fabric following outdoor exposure.

Weathering exposure in months	*Breaking strength in pounds after soil burial in weeks*			
	0	*4*	*8*	*12*
0	75	84	88	86
2	78	83	84	80
4	79	77	75	66
6	73	76	76	60
8	76	73	60	52
10	70	70	70	30
12	70	70	65	44
14	74	66	45	20
16	63	55	19	15
18	57	37	14	0
20	55	53	24	—

After 20 months' exposure, however, the fabric still withstood more soil burial than would untreated fabric. This is surprising when it is considered that most of the resin had been removed by this time, and many fibers in each yarn were completely devoid of resin. When this fact is added to the observation that resin loss begins at the periphery of the fibers, it appears to be evident that resin does not protect cellulose from microbial attack by forming a mechanical barrier.

It is concluded from this study that measurable changes in nitrogen content, cuprammonium fluidity, stress-strain curves and rot resistance can be detected during weathering before any appreciable loss in tensile strength occurs. These studies are currently being extended to other types of resin-treated materials to determine whether any of these reactions will provide a short cut to the evaluation of resistance to weathering, which can be generally applied to materials of this type.

SOIL-BURIAL EXPOSURE——Fabric treated to contain 12% methylolmelamine by the formic-acid-colloid process is completely protected during soil burial for 64 weeks (Figure 6a). Either the small untreated spots on some of the fibers, shown in Figure 4, were not large enough to allow fungal penetration, or they were protected by the geometry of fabric construction. After 64 weeks, the fabric deteriorated rapidly, which appears to substantiate our earlier claim that the deterioration of treated fabric in soil burial is a two-phase process (7). In contrast to what occurs during outdoor weathering, the loss of tensile strength in soil burial occurs before most of the resin is lost and before the fabric is converted to a cuprammonium-soluble product (Figure 6b and Figure 6c). Diagrams drawn from photomicrographs of the buried fabric at the critical stage of 64 weeks are included in Figure 4. The loss of resin was again observed to begin at the periphery of the fibers, confirming the conclusion that microbiological resistance is not due to a mechanical barrier. As anticipated from

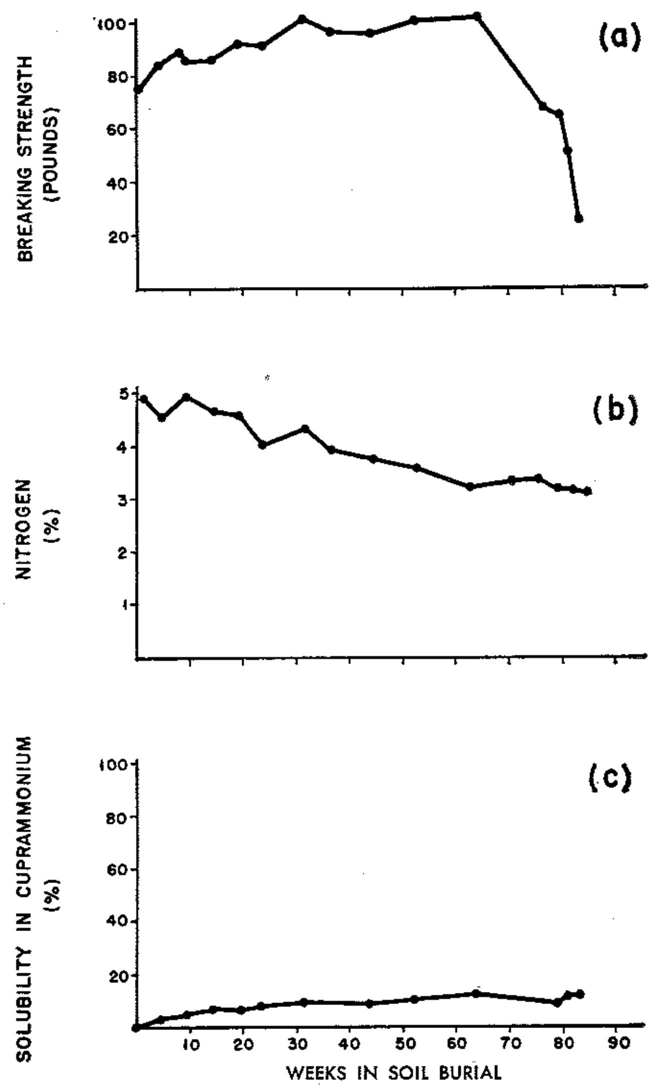

Figure 6
Effect of soil burial on: a) breaking strength; b) nitrogen content; and c) cuprammonium solubility of methylolmelamine-treated cotton duck.

the nitrogen content, the loss of resin had not proceeded as far in 64 weeks' burial as had been observed after 20 months' outdoor exposure.

Berard (2) noticed that soil burial of his treated fabric tended to reverse the initial loss of tensile strength that is presumed to be caused by the formation of crosslinks. It is seen in Figure 6a that the fabric completely regained its original breaking strength of 102 pounds before deterioration began. Therefore, the loss of breaking strength caused by the resin treatment does not necessarily indicate permanent damage since it is completely reversible. However, the regain in breaking strength is accompanied by only a partial regain in elongation at higher loads (Figure 7). Evidently, the decrease in breaking strength accompanying treatments of this type is not directly related to the observed decrease in elongation. If the loss of tensile strength is related to crosslinking, some of the stiffness which results in reduced elongation is not.

It can be concluded that the loss of nitrogen and the conversion to a cuprammonium-soluble product which occurred during weathering are primarily due to actinic effects since these effects do not occur in soil burial. An increase in elongation during stress occurred both in weathering and in soil burial, but in soil burial this change was even less marked than the change in breaking strength. Whether the physical and chemical

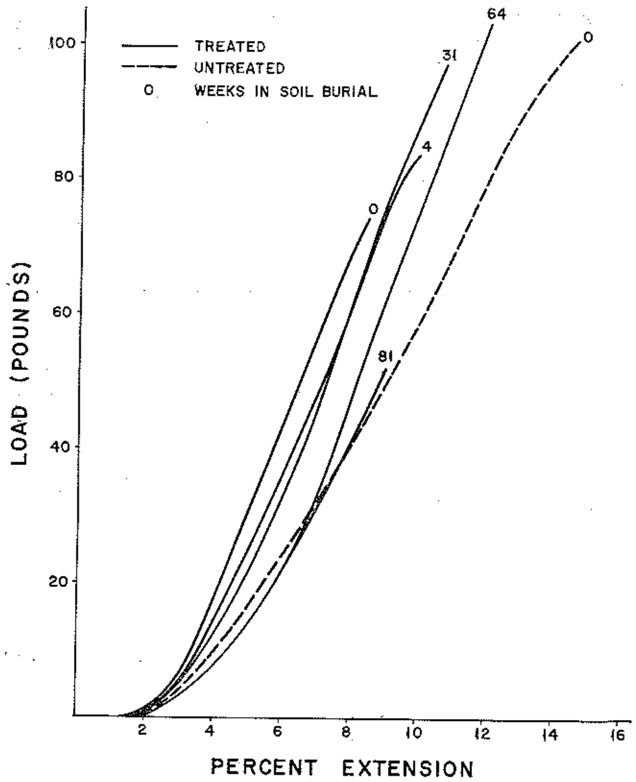

Figure 7
Changes in the load-elongation curve of methylolmelamine-treated cotton duck during soil burial.

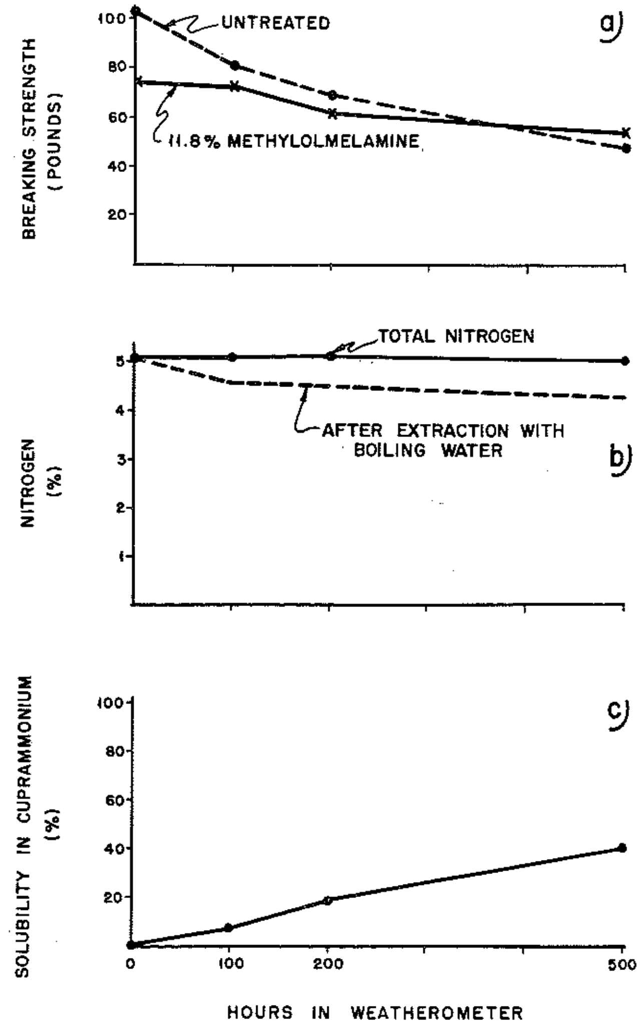

Figure 8
Effect of exposure in a Weather-Ometer on: a) breaking strength; b) nitrogen content; and c) cuprammonium solubility of methylolmelamine-treated cotton duck.

changes caused by actinic effects are related to the loss of microbial resistance during outdoor exposure is not certain. Unfortunately, none of the reactions studied appear to be related to the mechanism of rot resistance in soil burial; and thus do not fulfill the goal of an index of microbiological resistance that can be studied before the gross change in tensile strength is observed.

This points up the need for further research to determine the fundamental mechanism of microbiological resistance in modified cellulose before the evaluation of this type of material in soil burial can be based on the kinetics of disruption of the resistant mechanism.

WEATHER-OMETER EXPOSURE——These studies were undertaken to obtain data on the changes occurring during actinic degradation in the Weather-Ometer and to compare these with the changes that occurred in outdoor exposure. It was hoped that a more detailed comparison between the two types of exposure would be possible when the rate of nitrogen loss, solubility in cuprammonium hydroxide, and stress-strain curves are considered in addition to breaking-strength loss.

Breaking-strength data (Figure 8a) show that treated and untreated fabrics are essentially the same after 500 hours in the Weather-Ometer. On the basis of tensile strength, exposure of treated material for 500 hours in a Weather-Ometer is equal to 20 months' outdoor weathering at Maynard, Mass (Figure 3). However, on the basis of cuprammonium solubility, 500 hours in a Weather-Ometer is equal to only 4.5 months' outdoor weathering (Figure 8c). Since the Weather-Ometer was operated without the water-leaching cycle, the nitrogen content remained unchanged. However, some of the nitrogen had been converted to a form which was extractable with boiling water. On the basis of the nitrogen remaining after extraction, as shown in Figure 8b, 500 hours in a Weather-Ometer is also equivalent to only a few months' outdoor weathering. This is more in agreement with the cuprammonium solubility data than with the breaking-strength observations.

In direct contrast to outdoor weathering, the stress-strain curves of both treated and untreated fabric are essentially unaltered by 500 hours in the Weather-Ometer (Figure 9), even though considerable tensile strength loss occurred in both cases.

Evidently, exposure in a Weather-Ometer under these conditions, particularly in the absence of a water-leaching cycle, is not analagous to outdoor weathering. Consideration of the available data indicates that these two types of exposure may differ primarily in their effect on the crosslinks introduced by the resin treatment. The ability of the fabric under study to regain strength in soil burial is concluded to be due to the rupture of crosslinks. No regain in tensile strength occurred during outdoor weathering, although crosslinks were being broken, if the increase in elongation can be used as evidence. It can also be seen in Table I that the fabrics weathered for a few months possess the latent capability to regain strength, when placed in soil burial. The ability to regain strength when placed in burial was last observed in the fabric weathered for six months. This six-month interval corresponds to the exposure required for the original elongation to be regained (Figure 5).

It is therefore postulated that the observed change in breaking strength during outdoor weathering is actually the resultant vector of two opposing reactions; namely

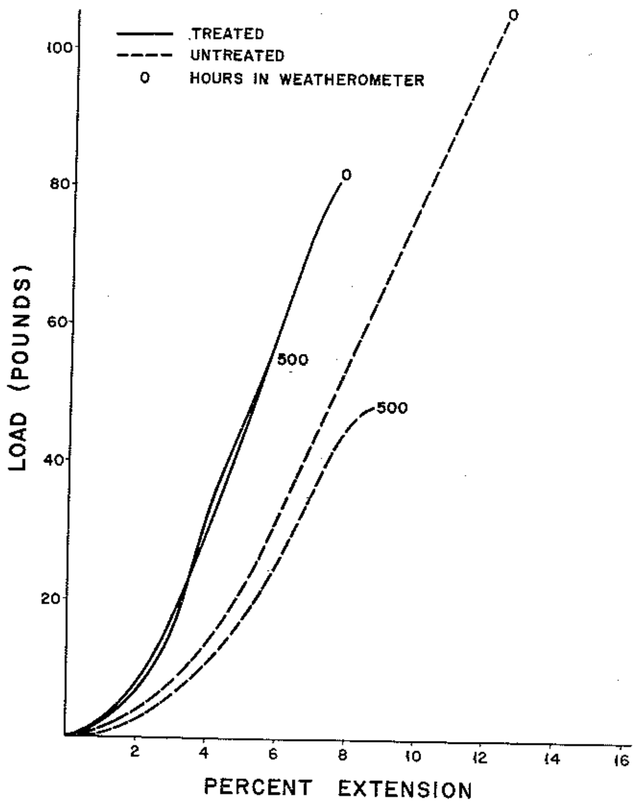

Figure 9
Effect of exposure in a Weather-Ometer on the load-elongation curve of untreated and methylolmelamine-treated cotton duck.

1) the breaking of crosslinks, which increases breaking strength, and 2) actinic degradation, which lowers strength. If this is true, the full measure of actinic degradation in outdoor exposure is not obvious from the slow rate of breaking-strength loss because of the opposing tendency to regain strength as crosslinks are broken. This view is supported by measurement of cuprammonium fluidity, which can be made only after the material has become completely soluble, but which was found to be 28 rhes after 22 months' exposure. This material, therefore, had apparently been degraded about 50%, rather than the observed change from 75 to 53 pounds, which is only 30%. It is concluded, therefore, that the net strength loss includes one vector tending to return the fabric from 76 pounds to its original strength of 102 pounds as crosslinks are broken; and that the actual vector for actinic deterioration is equivalent to a loss of 50%, or from 102 to 53 pounds.

In the Weather-Ometer, the stress-strain curve remains unchanged. If this means that no crosslinks are being broken, the observed rate of tensile loss may be greater than the observed loss during outdoor weathering because it is not modified by the opposing tendency to gain strength. Although this hypothesis could explain the difference between the two types of exposure, it does not explain why crosslinks are broken during outdoor exposure and not in the Weather-Ometer. It is possible that the increase in elongation during outdoor exposure requires water leaching which was not present in the Weather-Ometer; or the observed difference may reflect an inherent difference in the quality of radiation received. This problem will be investigated further using similar systems which are not originally crosslinked.

SUMMARY

Cotton duck is made completely resistant to microbiological attack in soil burial for 64 weeks when treated to contain 12% methylolmelamine by the formic-acid-colloid process developed by Berard (*1*). In fact, during this period, the material regains the tensile strength which is lost during the treatment. This performance should be compared to the maximum protection of 60 to 90 days in soil burial, which can be obtained by economical levels of the best add-on textile fungicides.

Berard's claim that this fabric was resistant to outdoor weathering at New Orleans, La, is substantiated. Cuprammonium fluidity was used to establish the mode of deterioration of untreated fabric in the same location, and prove that the observed weather resistance of treated fabric is indicative of protection against actinic effects and not merely another indication of rot resistance. In a long-term outdoor exposure test at Maynard, Mass, untreated fabric lost ⅓ of its original breaking strength in two months. Treated material lost ⅓ of its strength in 21 months. This methylolmelamine treatment did not afford the same degree of protection in a Weather-Ometer as in outdoor exposure; but an explanation for this effect is offered, based on the degree of rupture of crosslinks.

Changes in resin-nitrogen content, load-elongation curves and solubility in cuprammonium hydroxide show some of the differences between the reactions involved in outdoor weathering, soil burial and exposure in the Weather-Ometer. Originally, the treated fabric contained about 5% nitrogen and was completely insoluble in cuprammonium hydroxide. After 20 months' outdoor exposure, the material contained less than 1% nitrogen and was completely soluble in cuprammonium. These radical changes must be indicative of weather damage, and the physical loss of resin may account for the reduced resistance to microbiological attack which was observed. However, they are not directly related to the mechanism of rot resistance operative in soil burial. Both of these reactions had proceeded further in 20 months' outdoor exposure than in 81 weeks' soil burial; but the fabric in soil burial had been severely degraded by microorganisms while the weathered fabric was still somewhat resistant.

The physical loss of resin-nitrogen is concluded to be due to water leaching because no resin was lost in the Weather-Ometer without leaching. What converts the resin to a water-soluble form is unknown, since it occurred in the Weather-Ometer in the absence of microorganisms and, although to a lesser extent, it also occurred in soil burial in the absence of actinic effects. It could be concluded from the weathering experiments that the conversion to a cuprammonium-soluble product is a necessary prerequisite to nitrogen loss; because this conversion is complete before all the nitrogen is gone. On the other hand, these two reactions could be independent; because in soil burial, 40% of the resin-nitrogen is lost while no more than 10% of the fabric has become cuprammonium soluble.

In both soil burial and outdoor weathering the loss of nitrogen appears to begin at the periphery of the fibers, as judged from the ability to take up direct dyes. The periphery of many fibers was exposed without impairing microbial resistance. This observation indicates that the mechanical barrier theory of microbiological resistance is untenable, but it becomes even more difficult to visualize any relationship between nitrogen content and microbiological resistance.

Changes in the stress-strain curves can be used in the study of deterioration processes in those resin-treated fabrics where the treatment causes a decrease in elongation at all loads less than breaking strength. During outdoor weathering, the elongation of the treated fabric at a given load increases and eventually surpasses the elongation of untreated unexposed material. This elongation also increases during soil burial, but the fabric is deteriorated before all the elongation lost in the treatment has been recovered. In the Weather-Ometer, the breaking strength is decreased but the shape of the load-elongation curve is unchanged in both the treated and untreated fabrics.

These methods of studying the processes of deterioration are currently being applied to other resin-fabric systems. In outdoor exposures, particular emphasis is being placed on the change in cuprammonium solubility, because of the high precision possible with this method, and the rapid change in this property which occurs before gross changes in breaking strength can be observed. Further study is required to determine the mechanism of rot resistance in soil burial and develop a sensitive index of the reactions occurring in the first phase of deterioration in which no loss of breaking strength occurs. The use of the Weather-Ometer in the evaluation of this type of treatment is not recommended; not because the rate of breaking strength loss is not comparable to outdoor exposure, but because the whole process of deterioration may be markedly different.

ACKNOWLEDGMENTS

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